COMPARISON OF DETONATION VELOCITIES AND AVERAGE VIBRATIONAL MOTION OF ATOM PAIRS IN ORGANIC EXPLOSIVES

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Studies of the kinetics of fast condensed-phase reactions in organic systems show a reaction propagation "anomaly" in which the first-order reaction rates of many organic materials in the temperature range 3000-5000 K approach about 10^6 s^{-1}, even though the low-temperature decomposition rates are very different and the high-temperature rates are much lower than extrapolation of the Arrhenius plots would suggest. Vibrational frequencies and structural parameters obtained from infrared spectroscopy and x-ray data can be used to obtain an average velocity for the constituent atoms in the molecular system. Using Morse potential curve parameters for ten diatomic pairs, we have calculated in each case the frequencies for a number of lower-lying vibrational energy levels, corresponding to temperatures in the range from 3000 to 5000 K where detonations proceed. We discuss the apparent correlation between the detonation velocities of organic high explosives and the relative vibrational velocities and structural parameters of the bonds examined.

INTRODUCTION

Studies of the kinetics of very fast reactions (high-temperature decompositions, shock-tube reactions, and high-explosive detonations) have shown a reaction propagation "anomaly" in which the first-order reaction rates of organic materials in the temperature range 3000-5000 K all appear to approach about 10^6 s^{-1}. The reasons this phenomenon is termed an anomaly are that (1) the low-temperature decomposition rates of many such materials studied[1,2] are very different from each other, and (2) the high-temperature rates are much lower than extrapolation of the Arrhenius plots would suggest.

One explanation proposed[3] is that there is an atomic vibration velocity "barrier" somewhat analogous to the sonic (translation velocity) "barrier." This can be deduced from infrared spectroscopy and x-ray crystallography of the organic materials of interest[3] (by observing effects associated with the C-H, N-H, and O-H bonds), using a simple calculation,

$$V = \nu c u, \qquad (1)$$

where V is the average vibrational velocity, ν is the infrared frequency (in cm^{-1}) of the par-

ticular bond vibration, c is the velocity of light, and u is the distance moved by an atom relative to its bond-mate in one vibration period. A second method for calculating these values is presented in this paper.

CALCULATIONAL METHOD

The average atomic vibrational velocities can also be calculated through the use of a least-squares fit of diatomic potentials to Morse or Hulbert-Hirschfelder functions. We selected ten atomic pairs found in organic explosives and calculated the vibrational frequencies for all of the energy levels considered. From these frequencies and the distances, at each energy level, of the relative motion of the atoms, it is again a simple calculation to obtain the average vibrational velocities at each energy level. Examples are illustrated in Figs. 1 and 2 for the H-H pair[4] and in Table 1 for the C-H pair.

The two equations used are as follows:

$$\nu = c[(\omega_e - \omega_e x_e) - 2\omega_e x_e v], \qquad (2)$$

where c is the velocity of light, ω_e is the classical vibrational frequency for an infinitesimal amplitude of motion of an anharmonic oscillator, $\omega_e x_e$ is the measure of the anhar-
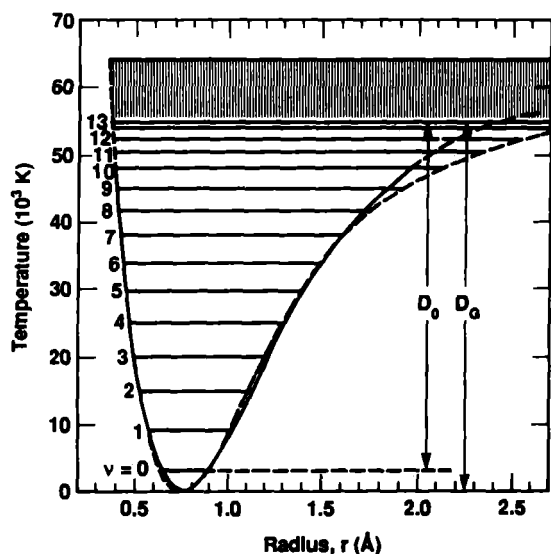
FIGURE 1
Potential curve of the H_2 ground state with vibrational levels. The broken curve is a Morse function, and the full curve is from experimental data. End points of the vibrational levels correspond to the classical turning points of the vibration. In quantum theory these sharp turning points are replaced by broad maxima of the probability amplitude ψ. (After Herzberg.[4])
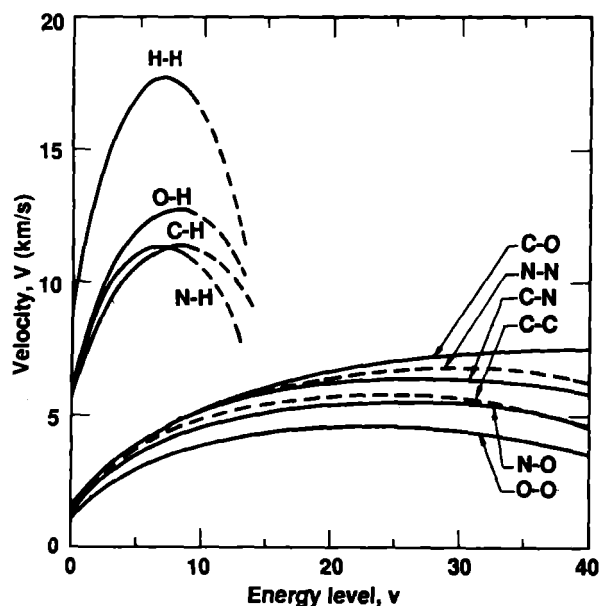

FIGURE 2
Plot of average vibrational velocity vs energy level for the ten atom pairs considered here.

monicity of the oscillator, and v is the vibrational quantum number;

$$V = 2d\nu, \qquad (3)$$

where V is the average vibrational velocity (as above), d is the distance between the sides of the potential curve at a given energy level v, and ν is the vibrational frequency (in s^{-1}).

TABLE 1
Data illustrating calculation of the average relative vibrational velocities for the C and H atoms in a C-H bond.

v	ν (s^{-1})	d (Å)	V (km/s)
0	8366.8	0.2329	3.896
1	7949.3	0.4022	6.394
2	7531.8	0.5345	8.051
5	6279.4	0.8520	10.700
10	4192.0	1.3759	11.536
15	2104.6	2.1327	8.977

DISCUSSION

The velocity curves for the ten atomic pairs considered here are given in Fig. 2. There is a satisfying correlation in all the curves.

It is interesting that there is a maximum average velocity in each curve at a point near the central energy level calculated, and that for the coupled heavier atoms the velocity does not change very much in a large central portion of the curves.

For our kinetics studies in high explosives, the average vibrational velocities in the temperature range of 3000-5000 K are important.*

In Table 2 and Fig. 3, velocity values in this temperature range are shown for the ten atomic

*For very high "temperatures" (i.e., high energy levels), the Morse function will not be as good a fit to the experimental data. Thus the derived vibrational motion will be less reliable. However, the calculational results should be reasonable in the temperature range 3000-5000 K.

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pairs considered. It is seen that the values for C-H, N-H, O-H, and H-H are in the range of detonation velocities of the organic high explosives (about 4-9 km/s). When one considers that the shock wave energy in a detonation would add to this average velocity and that the maximum velocity at each energy level could be a little higher than the average, there is a correlation here strongly indicative of a vibrational velocity "barrier" in high-temperature reactions, as seen in our earlier work.[3,5]

One other interesting observation is illustrated in Table 3, where the energies (or "temperatures") associated with the maximum average velocities for each atom pair are listed. For C-H, N-H, and O-H the temperatures range from 30,037 to 38,921 K (2.59 to 3.35 eV), the maximum average velocities from 11.6 to 13.0 km/s.
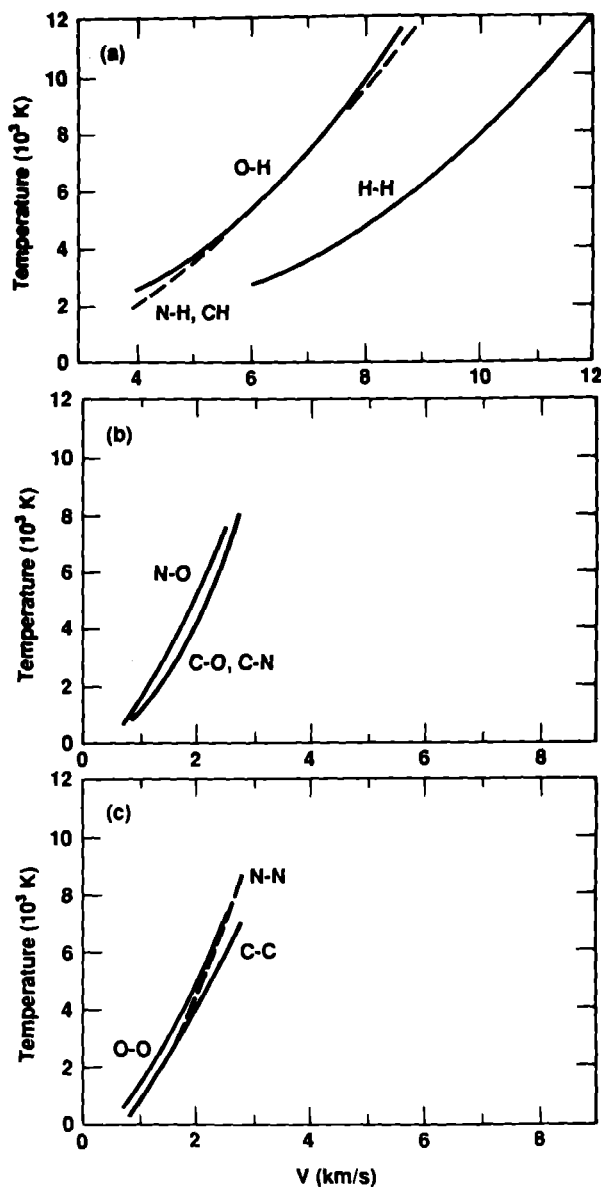
TABLE 2
Average vibrational velocities for the ten atom-pairs at temperatures of 3000-5000 K.

Atom pair	Average vibrational velocity (km/s) at:				
	3000 K	3500 K	4000 K	4500 K	5000 K
H-H	6.40	6.92	7.45	7.85	8.20
O-H	4.49	4.95	5.25	5.65	5.92
N-H	4.65	5.02	5.35	5.69	5.98
C-H	4.62	5.00	5.35	5.65	5.93
O-O	1.57	1.71	1.82	1.96	2.02
N-O	1.50	1.62	1.75	1.81	1.99
C-O	1.71	1.82	1.98	2.11	2.20
N-N	1.72	1.82	1.96	2.07	2.20
C-N	1.71	1.88	2.01	2.12	2.25
C-C	1.70	1.81	2.00	2.12	2.26

TABLE 3
The temperature at the maximum average vibration velocity for each atom pair.

Atom pair	V_{max} (km/s)	Temp (K)
H-H	18.1	37,257
O-H	13.0	38,921
N-H	11.6	30,685
C-H	11.7	30,037
O-O	4.75	44,086
N-O	5.5	53,967
C-O	7.5	95,759
N-N	7.0	80,202
C-N	6.5	66,746
C-C	6.0	52,261

FIGURE 3
Plots of average vibrational velocities as a function of temperature.

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For the heavier couples, these values range from 44,086 to 95,759 K, while the maximum average velocities only reach 4.75 to 7.5 km/s. The persistence of these relatively low velocities at the very high temperatures can, of course, be directly correlated with such parameters as the binding energies, reduced masses, and anharmonicities of the diatomic pairs. We also observed in our molecular dynamics calculations that shock velocity at lower temperatures was a rather weak function of temperature.[5]

Another significant observation with regard to detonation phenomena is that diatomic hydrogen (H-H) has significantly higher vibrational velocities than all the other atom pairs considered. It has been observed that explosives with a high atomic percent of hydrogen generally have relatively high detonation velocities compared to the values calculated from thermodynamic properties. As seen here, at 37,257 K, H-H shows a velocity of about 18.1 km/s.

CONCLUSIONS

There is a remarkable stability of the average vibration velocities in the atom pairs associated with organic materials as they are raised to very high temperatures (about 30,000 to 100,000 K). In the range from 3000 to 5000 K, where detonations proceed, the vibrational velocities of the C-H, O-H, N-H, and H-H atomic pairs are very near the detonation velocities of organic high explosives. The results here correlate very well with those obtained earlier[3] with Eq. (1).

REFERENCES

1. H. Eyring, Science 199 (1978) 740.

2. F. E. Walker, Physical Kinetics, Lawrence Livermore National Laboratory, Livermore, Calif., UCRL-93642 (November 21, 1985). Submitted to Journal of Applied Physics.

3. F. E. Walker, Propellants and Explosives 6 (1981) 15.

4. G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules (Van Nostrand Reinhold, New York, 1950), p. 99.

5. A. M. Karo et al., The study of shock-induced signals and coherent effects in solids by molecular dynamics, Lawrence Livermore National Laboratory, Livermore, Calif., UCRL-85576 (August 31, 1981).